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Part I

EXPLORATORY DEVELOPMENT OF HEAT RESISTANT AND NONFLAMMABLE FIBROUS MATERIALS

TECHNICAL REPORT AFML–TR–74–65, PART I

MAY 1974

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT–PATTERSON AIR FORCE BASE, OHIO 45433

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This report was prepared by Fabric Research Laboratories, Dedham, Mass. under U. S. Government Contract No. F33615-73-C-5034. The work was initiated under Project 7320, "Fibrous Structural Materials," and was conducted from January 2, 1973 through January 31, 1974. It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, with Mr. Stanley Schulman acting as project engineer.

Mr. Norman J. Abbott was the FRL director responsible for the overall program. The dyeing and thermal stabilization studies were carried out by Mr. Joseph S. Panto. The authors wish to express their appreciation to Dr. Milton M. Platt for handling contractual matters and many helpful discussions throughout the course of the work.

This report is submitted by the authors in March 1974.

This technical report has been reviewed and is approved.

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A treatment which protects thermally stabilized polybenzimidazole (PBI) from the effects of repeated laundering was developed, providing retention of stability through 15 wash-dry cycles in alkaline detergent.

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SECTION I

INTRODUCTION AND SUMMARY

During the past several years, FRL has been associated with the Air Force Materials Laboratory's development of the PBI (polybenzimidazole) fiber. We have studied the properties of the fiber; woven or knitted a wide variety of fabrics from it; developed procedures for dyeing it; and developed a treatment which prevented it from shrinking when exposed to a JP-4 fuel fire for 3-6 seconds. The latter treatment involved the uptake of substantial amounts of acid which subsequently could be partially removed when the treated material was washed in certain detergents. One project undertaken during the past year of the current contract was to study the effect of laundering on the thermal stability of treated PBI, and to develop a means of improving the durability of the acid treatment through at least 15 laundering cycles.

SECTION II

THERMAL STABILIZATION OF PBI FABRIC

The thermal stabilization treatment which FRL developed for PBI fabrics involves treatment with an acid, usually sulfuric, at quite high levels of add-on. These levels are needed to reduce the shrinkage in a 3-6 second exposure to a JP-4 fuel flame to an acceptably low level. The shrinkage usually taken as being acceptable is no more than 4% in warp and filling directions. This is based on the requirements of MIL-C-43600A, which specifies maximum shrinkage of 4% in the warp and 1.5% in the filling after 15 launderings of a flight suit fabric. Such a shrinkage is just visually perceptible and is considered to be acceptable for flight suit applications. Untreated PBI fabric shrinks approximately 50% in each direction when exposed to a JP-4 fuel fire without imposing any latent restraints. Properly stabilized fabric shrinks no more than approximately 1% under similar exposure conditions.

The effectiveness of the acid treatment is not altered by leaching in water. For example, in 15 standard laundering cycles in a machine containing only distilled water, no change in thermal shrinkage results. The addition of a detergent, however, most of which are alkaline, may drastically reduce the thermal stability of the fabric.

A study was made to determine the resistance of acid treated PBI fabric to laundering in various types of detergents, and a treatment was developed which stabilizes the treated fabric so as to make it resistant to 15 washes in a standard home-type automatic washer.

1. Laundering of Thermally Stabilized PBI Fabric

Twenty-three, home-type detergents were purchased off the shelves of a supermarket and PBI fabric which had received the thermal stabilization treatment was washed up to 15 cycles with each of these detergents using a standard home-type automatic washing machine and tumble dryer. Measurements of the thermal shrinkage were made after 5, 10, and 15 cycles. For an initial screening after 5 and 10 cycles an FRL test involving exposure of the specimen for 3 seconds to the flame of a Meker burner adjusted to the level of 2.5 calories per square centimeter per second was used. Those specimens were exhibited an average linear shrinkage of more than 4% in this test were removed from the study and the detergent in which they were washed was no longer used. Those specimens which remained through 15 cycles of washing were sent to AFML for standard AFML JP-4 fuel burner test.

The results of these measurements, as well as the amount of shrinkage which occurred during laundering, are given in Table 1. Two of the detergents, Arm & Hammer and 20 Mule Team, were so severe that 5 cycles of washing almost completely eliminated the effects of the acid treatment. Table 1 also includes values showing the resistance of a Nomex II flight suit fabric to laundering in Arm & Hammer detergent.

TABLE 1

THE EFFECT OF LAUNDERING ON THE THERMAL STABILITY OF SULFURIC ACID STABILIZED PBI FABRIC

Product Name	Average Linear Thermal Shrinkage (%) After 5[1] Cycles	After 10[1] Cycles	After 15[2] Cycles	Laundering Shrinkage (%) 5 Cycles Warp	Fill	10 Cycles Warp	Fill	15 Cycles Warp	Fill
Untreated PBI Fabric (not washed)	50	49	--						
Stabilized (not washed)	1	1	3						
Distilled water	1	1	1	2.3	0.0	4.6	0.0	4.6	1.7
Tide	0	3	25	4.6	1.7	4.6	1.7	2.3	1.7
Oxydol	2	6	--	2.3	0.0	2.3	0.0	---	---
Ivory Flakes	2	3	36	2.3	1.7	4.6	3.4	4.6	1.7
Bold	1	4	26	2.3	0.0	4.6	1.7	4.6	1.7
Ajax	1	2	23	2.3	1.7	2.3	0.0	4.6	1.7
Fab	2	1	20	2.3	0.0	2.3	1.7	4.6	1.7
Gain	3	3	17	0.0	0.0	2.3	1.7	4.6	1.7
Cheer	1	3	34	4.6	1.7	4.6	1.7	4.6	1.7
Cold Power	2	3	23	2.3	0.0	2.3	1.7	4.6	0.0
Arm & Hammer	34	--	--	4.6	1.7	6.7	1.7	---	---
20 Mule Team	28	--	--	4.6	1.7	4.6	3.4	---	---
Burst	2	9	--	2.3	0.0	2.3	1.7	---	---
All	1	13	--	0.0	1.7	2.3	1.7	---	---
Dash	0	8	--	2.3	0.0	2.3	1.7	---	---
Drive	2	6	--	0.0	0.0	2.3	0.0	---	---
Dreft	2	15	--	2.3	1.7	2.3	0.0	---	---
Punch	2	7	--	2.3	0.0	2.3	0.0	---	---
Instant Fels	0	10	--	4.6	1.7	4.6	1.7	---	---
Bonus	2	5	--	2.3	1.7	4.6	0.0	---	---
Rinso	2	5	--	2.3	0.0	4.6	1.7	---	---
Silver Dust	1	2	13	0.0	0.0	2.3	1.7	4.6	1.7
Wisk	1	3	10	0.0	0.0	2.3	0.0	4.6	1.7
Duz	0	2	30	2.3	1.7	2.3	0.0	4.6	1.7
Nomex II Fabric									
Arm & Hammer	-2[3]	-2[3]	0	-4.8[3]	0.0	0.0	-3.6[3]	-2.3[3]	-3.6[3]

[1]FRL Test, [2]WPAFB Test, [3]Growth.

Measurements of solution pH indicated that initially all of the detergents gave pH values within the range 9.5 to 10.6. After washing the pH of the wash liquor was generally in the range of 7 to 8. The main exception to this was Ivory Flakes, where even after 15 cycles the wash liquor had a pH of only 9.1. In spite of this, the fabric washed in Ivory Flakes showed excessively high thermal shrinkage after 15 launderings. Presumably, this soap was absorbed by the fabric during washing and acted as a fuel during exposure to the flame test.

The weight loss of the fabric specimens was also determined and it ranged from about 8 to 12%.

A check of the resistance of the thermal stabilization treatment to dry cleaning indicated that 15 dry cleanings had no serious effect on the thermal stability of the fabric.

2. Phosphoric Acid Treatment of PBI

Phosphoric acid can be used in place of sulfuric to provide thermal stability in PBI fabric and has the added advantage that the LOI index is raised to a very high level. PBI fabric treated with phosphoric rather than sulfuric acid was washed in distilled water and in 2 selected detergents in order to determine whether this treatment had a greater resistance to washing than the more usual sulfuric acid treatment. The thermal shrinkages obtained in the FRL test after 5 cycles of washing are given in Table 2. It is clear that even the use of distilled water drastically reduced the thermal stability of PBI and that apparently the use of phosphoric acid has nothing to offer in preference to the use of sulfuric acid.

TABLE 2

THE EFFECT OF LAUNDERING ON THE THERMAL STABILITY OF PHOSPHORIC ACID STABILIZED PBI FABRIC

Product Name	Linear Thermal Shrinkage (%) After 5 Laundering Cycles
Distilled Water	31
Tide	19
Gain	20
Duz	31

3. Dynatech Treatment

Another treatment which offers some degree of thermal stability is that developed by Dynatech Corporation. Fabric so treated was washed in two selected detergents and the residual shrinkage measured in the FRL test. The results are given in Table 3. The fabric washed in Duz retained good thermal stability although it burned vigorously when expoed to a flame after 5 wash cycles. Resistance to washing in Arm & Hammer detergent was unsatisfactory.

TABLE 3

THERMAL SHRINKAGE OF PBI FABRIC TREATED WITH THE DYNATECH PROCEDURE AFTER 5 AND 10 LAUNDERING CYCLES

	Linear Thermal Shrinkage (%)	
Detergent	5 Washes	10 Washes
Duz	2*	0*
Arm & Hammer	8	20

*Surface of specimen burned vigorously.

4. Heat Treatments

It is clear from all of these measurements, that the usual treatments used to provide thermal stability in PBI fabric, have poor resistance to laundering. Our work proceeded, therefore, to attempt to develop a means of stabilizing the acid treatment in order to provide adequate laundering resistance.

There was reason to believe that the use of a high temperature heat treatment after the acid treatment would improve the ability of the fabric to retain the acid through multiple launderings. Initial experiments using temperatures as high as 250°C and times as long as 3 hours provided only marginal improvement. It was finally determined that exposure of the sulfuric acid treated fabric in an oven at 350°C for from 5 to 15 minutes enabled the fabric to retain its high level of thermal stability through 15 washes in Arm & Hammer detergent. Because of differences in sample sizes and in oven characteristics, it was felt that the best criterion to be used in any large scale treatment would be to match the color with that of a fabric specimen which had been exposed under ideal conditions in a small oven for 15 minutes at 350°C. This criterion was used in treating large quantities of fiber under another Air Force contract (F33615-73-C-5134) with satisfactory results.

SECTION III

SCOURING AND CALENDERING OF STAPLE DYED PBI FABRIC

A study was initiated to determine the extent to which the appearance and hand of stock dyed PBI fabric could be improved by calendering. Several samples of fabric were calendered at Kenyon Piece Dye Works, Inc., Kenyon, Rhode Island. In each case a 1/4 yard piece of fabric was placed between the open nip of a steel and plastic roll. The nip was then allowed to close so that only 1/2 of the sample was calendered. This procedure was repeated to show the effect of using 20, 40 or 60 tons pressure on the appearance and hand of the fabric. Upon examination of the samples the project engineer agreed that the use of 40 tons pressure produced a fabric which had a more uniform surface appearance, less surface fuzz and a more pleasing sheen than uncalendered fabric. These calendering conditions were subsequently used to process several hundred yards of fabric under another program (F33615-73-C-5134).

SECTION IV

EXPERIMENTALLY WOVEN FABRICS FROM STOCK DYED FIBER

Work done under contract F33615-71-C-1287 produced small quantities of 37/2, 40/2, and 44/2 yarn, spun by Textile Research Services, Inc., from heat stabilized and dyed PBI fiber. A 4.5 oz/yd^2, 2/1 twill fabric was then woven by TRS from the 37/2 yarn, and 11 yards delivered to FRL where it was tested, and a sample forwarded to AFML for evaluation. Since then, FRL has woven a similar fabric from short warps made from the 40/2 and the 44/2 yarns.

Physical and mechanical properties of these materials were measured and are listed in Table 4, along with the values previously obtained for the 37/2 fabric.

It was decided that the fabric made from 37/2 yarn had the best characteristics for a flight suit fabric, and this construction was used in another contract (F33615-73-C-5134) which called for the manufacture of 500 flight suits.

TABLE 4

PHYSICAL AND MECHANICAL PROPERTIES OF 2/1 TWILL FABRICS WOVEN FROM STOCK DYED PBI FIBER

Identification Number	Yarn Size and Ply (cc)[1]	Ends per Inch	Picks per Inch	Weight (oz/sq yd)	Air Permeability[2] (cu ft/min/sq ft)	Rupture Load[3] (lb/inch)		Rupture Elongation (%)		Tearing Strength[4] (lb)	
						Warp	Fill	Warp	Fill	Warp	Fill
69124-101-49	37/2	59	56	4.6	132	54	51	30	24	6.2	---
69124-101-50	40/2	65	65	4.8	77	54	56	29	30	5.3	6.1
69124-101-51	44/2	72	66	4.6	64	55	51	31	26	5.3	5.6

[1] Cotton count
[2] At 0.5" water pressure differential
[3] Ravelled strip method
[4] Tongue-tear method.

SECTION V

MOISTURE REGAIN OF PBI AND HT-4 FABRIC

The moisture regain of two fabrics, a staple dyed and treated PBI fabric and an HT-4 fabric, were determined according to ASTM Test Method D 2654 at 70°F and 35, 50, 65, and 95% relative humidity. The specimens were conditioned in the Aminco Aire Chamber for more than 48 hours at each humidity setting. Three specimens of each fabric were exposed. The values obtained are given in Table 5 and are plotted in Figure 1, which shows a linear relationship between moisture regain and relative humidity over the range of measurement.

TABLE 5

MOISTURE REGAIN OF TREATED PBI AND HT-4 FABRICS

Fabric	RH	Moisture Regain (%) at 70°F 32-35%	50%	65%	95%
PBI (69124-101-49, staple dyed and treated)		9.9	12.9	14.8	20.0
		9.8	12.9	14.9	20.1
		10.4	13.4	15.0	30.5
	Avg.	10.0	13.1	15.0	20.2
HT-4 (72753-101-10)		4.3	6.1	7.4	11.0
		4.2	6.1	7.4	11.0
		4.1	6.1	7.5	11.0
	Avg.	4.2	6.1	7.4	11.0

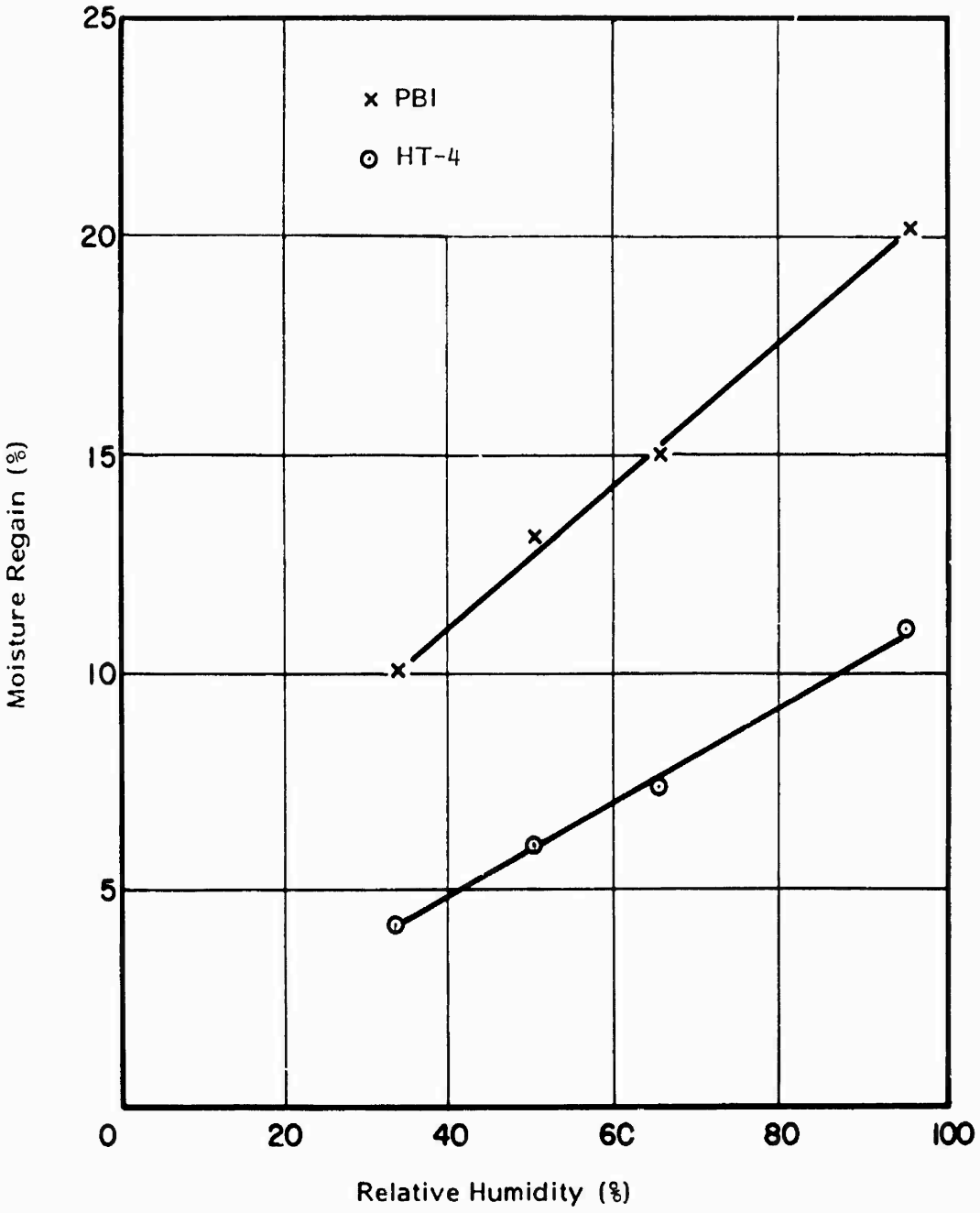

Figure 1. Moisture Regain as a Function of Relative Humidity to PBI and HT-4 Fabric

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